

Phosphorus Loss by Stream Transport from a Rural Watershed: Quantities, Processes, and Sources¹

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ABSTRACT

Loss of dissolved and particulate phosphorus by stream transport was determined over a 20-month period for Fall Creek, a stream draining a predominantly rural watershed of 330 km² in central New York. Samples were taken several times daily during most high flow periods and at 3 to 20 day intervals during low flow periods. Samples were usually processed within 4 hours since redistribution of P among chemical forms was rapid. Losses of P from the watershed per unit time varied by several orders of magnitude and 75% of the P loss occurred in the highest flow which occurred in 10% of the time. In reaches well downstream from major point source inputs, dissolved inorganic P concentrations were highest during storm events due to two processes: desorption of P accumulated in the bed sediment from point source inputs during low flow, and inputs from diffuse sources in surface runoff. Dissolved organic P concentrations were not correlated with flow. Approximately 20% of the dissolved P lost from the watershed was derived from diffuse sources associated with farming, 45% was derived from natural geochemical processes, and 35% from point source inputs. Less than 1% of the P applied to the landscape in chemical fertilizer and manure was lost from the watershed in dissolved form.

Additional Index Words: nonpoint source pollution, dissolved phosphorus, particulate phosphorus, land use, stream sampling.

The awareness of phosphorus in surface waters as a potential environmental quality problem has resulted in considerable research designed to measure P loss from watersheds by stream transport. Studies on several watersheds are reviewed by Ryden et al. (1973). Information beyond simple measurement of the P loss is useful; that is (i) information on the effects of various human activities on P losses, from which inferences can be made regarding the feasibility of various control measures, and (ii) knowledge about the amounts of the various chemical fractions of P (i.e., dissolved and particulate forms) transported by streams that are likely to have different effects on algae blooms, rooted aquatic plant growth, and other indices of cultural eutrophication.

The research described here was undertaken to measure the quantities of three operationally defined P fractions lost by stream transport from a watershed in central New York and to determine the influence of human activity on dissolved P loss.

In the following sections, the watershed is described, the patterns and timing of P loss from the watershed are presented, and the processes influencing the P content of the stream flow in this watershed are discussed. The loss of several P fractions is determined and procedures for estimating the influences of human activities are described.

WATERSHED CHARACTERISTICS

The Fall Creek watershed is located in central New York near Ithaca (Fig. 1). The drainage area above the main gaging station at location 1 is 330 km² and includes a human population of about 12,000 with about 30% centered in six small villages. About 80% of the area is

covered with acid soils derived from glacial till and about 20% of the area is covered with medium-lime soils derived from glacial outwash in valley areas. The landscape is hilly and dissected with a maximum relief of about 300 m. Many of the valley areas are filled with thick, non-continuous lenses of gravel outwash, and gently tilted strata of siltstone and shale comprise the bedrock throughout the watershed.

Major land use is given by Child et al. (1971) as 32% forest, 43% agricultural land, including pasture, and the remainder is described as abandoned agricultural land. Dairying is the major farming operation, with an average of one dairy with 55 cows per square mile. There is a secondary sewage treatment facility in the study area at Dryden that serves about 1,400 people and discharges its effluent into Virgil Creek, the main tributary to Fall Creek.

PHOSPHORUS FRACTIONS

Phosphorus transported by streams is distributed among a variety of chemical compounds in aqueous and solid phases. Phosphorus was fractionated by analytical procedures into three operationally defined categories: dissolved molybdate reactive P (DMRP), dissolved unreactive P (DUP), and solid phase P (SPP). DMRP is generally referred to in the literature as "ortho-P", "PO₄-P", "SRP", or soluble inorganic P, but since the molybdate methods may measure forms other than orthophosphate (Rigler, 1968), the descriptive terms are used here. DUP is probably comprised of organically bound phosphates and, below sewage outfalls, may include some condensed phosphates from detergents. SPP is comprised of a small labile portion that is readily exchangeable with inorganic P in solution plus a much larger and relatively inert fraction comprised of crystalline, occluded, and organic P. Crystalline forms transported by the streams in the Fall Creek basin are probably mostly iron and aluminum phosphates which are thermodynamically stable in most soils of the landscape, since the soils have a pH of 4-5. The effect of retention in the streambed where the pH is 8-8.5 is uninvestigated, but slow dissolution or transformation of these minerals is expected, since they are unstable under such pH conditions. Occluded phosphate may be present throughout the particulate matter and is released to the solution phase only through disintegration of the bulk solid phase.

METHODS

Samples were collected on an event basis, that is, frequently during storms with less frequent sampling during low flow periods. At the main sampling site (site 1, Fig. 1), several samples per day

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were collected during most high flow periods and at 3- to 20-day intervals during low flow periods. About 2,100 samples were collected between September 1972 and April 1974 from 30 locations in the drainage basin. Subwatershed sampling was concentrated in the Virgil Creek watershed since concentrations were usually highest in that area. Approximately 700 samples were collected at site 1 which is located near a U. S. Geological Survey gaging station from which bihourly discharge measurements were obtained. At this location, the stream flows over a low dam and through a narrow gorge. Sampling studies indicated that mixing is thorough and grab samples were representative of both suspended and dissolved loads.

Samples were collected by hand or with automatic samplers. The latter method was generally sufficient for sampling dissolved loads, but the automatic samplers did not obtain representative samples of suspended loads. A detailed discussion of preparation, storage, and analytical problems encountered is given by Johnson et al. (1975). Briefly, the analytical procedures were as follows. For analysis of dissolved P, samples were clarified by centrifugation at a relative centrifugal force of 35,000 g for 30 minutes. Centrifuged samples did not contain suspended material that interfered with DMRP determination. Processing and analysis were carried out within a few hours since redistribution among the various chemical forms was rapid, and neither freezing nor refrigeration of whole samples or supernatants prevented rapid changes in DMRP concentration.

DMRP was determined in supernatants by treatment with molybdate. The molybdate complex was extracted in isobutanol, reduced with SnCl_2 and the intensity of the resulting blue color was determined. Total dissolved phosphate (TDP) was determined in supernatants using the persulfate digestion procedure of Menzel and Corwin (1965), with subsequent colorimetric determination carried out using an autoanalyzer and the procedure of Fiske and Subbarow (1925). DUP is defined as the difference between TDP and DMRP.

Suspended solids were determined by weighing oven-dried (105°C) sediment after separation by centrifugation at 1,500 g for

30 minutes. SPP was determined by the $\text{Mg}(\text{NO}_3)_2$ method described by the Association of Official Agricultural Chemists (1955).

Labile P on storm sediment was estimated on selected samples from sorption isotherms using the method of Taylor and Kunishi (1971) with slight modifications. Sediment samples obtained by centrifugation at 35,000 g were equilibrated with Fall Creek water with appropriate additions of K_2HPO_4 . The sediment/solution ratio was the same as in the original stream sample and the equilibration period was 20 hours. Subsequent P analysis was carried out using the procedure described for DMRP.

In one experiment, streambed cores were collected in plastic tubes 1.5 cm in diameter to a depth of about 50 mm. Bicarbonate extractable P was determined using the procedure of Olsen et al. (1954). Whole cores were extracted, so the sediment/solution ratio varied somewhat around 1:20. Analysis was by the procedure described for DMRP with the acidity adjusted appropriately. Since the particle size distribution varied widely, mechanical analysis was carried out using the pipette method described by Day (1965). Results are reported on a percentage by weight of silt plus clay.

RESULTS

General Comments

Concentrations of DMRP at the gaging station (site 1) generally ranged from about 0-50 $\mu\text{g P/liter}$. At low flow, concentrations in samples collected averaged about 10 $\mu\text{g P/liter}$, increasing during storm periods to about 35 $\mu\text{g P/liter}$ or more (Fig. 2). Highest discharge and DMRP concentrations occurred during the periods extending from late fall through early spring. Approximately 50% of the DMRP was lost during 10% of the observation period; that is, during the period of highest flows.

DUP concentrations averaged about 12 $\mu\text{g P/liter}$ varying from about 0 to 75 $\mu\text{g P/liter}$. There was no well-defined, consistent relationship between DUP and discharge and no significant seasonal differences in concentration or variability.

Particulate forms were lost from the watershed almost exclusively during storms, to the extent that about 80% of this fraction was lost in 10% of the observation period. Concentration of particulate forms ranged from about 1

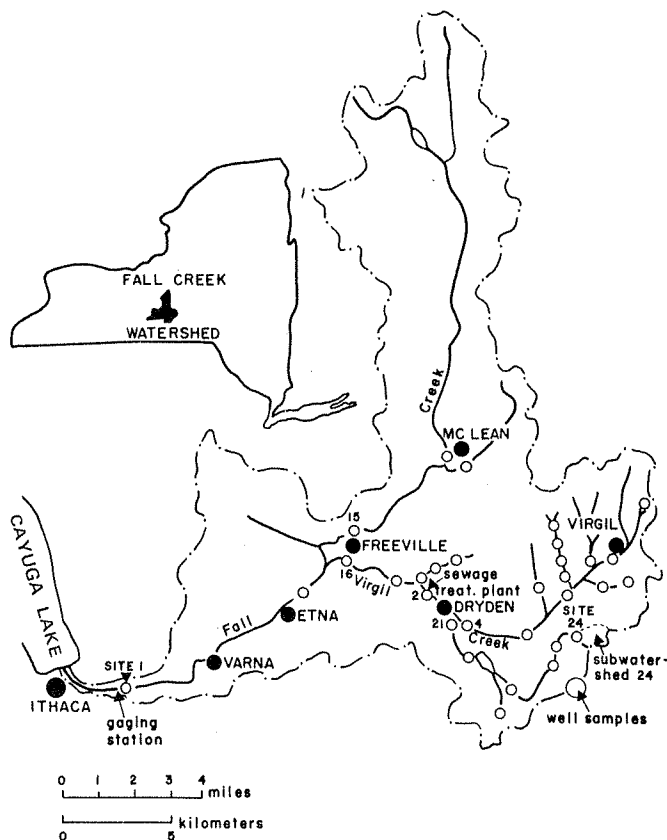


Fig. 1—Fall Creek watershed. Circles represent major sampling sites and numbers refer to sites discussed in the text.

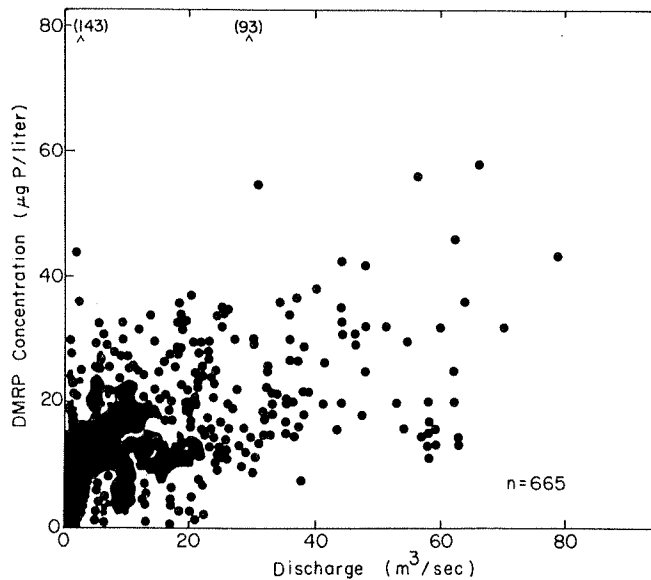


Fig. 2—DMRP concentration plotted against discharge at site 1 for the period September 1972 to April 1974, n = number of observations.

to 1,000 $\mu\text{g P/liter}$ of stream water. Percent P in the suspended solids remained relatively constant during storms, often increasing somewhat during low flow probably due to an increase in the P associated with the higher organic matter content of the suspended load. In Fig. 3, percent P of the suspended solids is plotted against suspended solids concentration for samples collected throughout the watershed.

Mean dissolved P concentrations measured at site 1 were about twice as high as the concentrations measured in ground water and in streams draining two forested sub-watersheds with no human activity. At site 2, 300 m below the Dryden sewage treatment plant, dissolved P concentrations exceeded 200 $\mu\text{g P/liter}$ at low flow. In other tributaries throughout the watershed, concentrations were generally $< 20 \mu\text{g P/liter}$ at low flow and .25-40 $\mu\text{g P/liter}$ at high flow.

The flow-duration relationship is illustrated in Fig. 4 for the stream at location 1. Also plotted are the cumulative losses of phosphorus, cumulative flow, and cumulative number of samples plotted against the percent of time a given discharge is exceeded. This illustrates that most of the runoff and P loss occurred in a relatively short timespan during which highest discharge rates occurred, and that the sampling was reasonably well distributed among all flow regimes.

Phosphorus Export

DMRP

At site 1, DMRP concentrations generally peaked slightly before peak flows in a given storm, and rate of change of flow was a useful variable in relating DMRP concentration to discharge measurements. Monthly equations of the form

$$\text{DMRP} = a_0 + a_1Q + a_2\Delta Q/\Delta t, \quad [1]$$

where

- DMRP = DMRP concentration in $\mu\text{g P/liter}$,
- Q = instantaneous discharge in m^3/second ,
- $\Delta Q/\Delta t$ = $\text{m}^3 \text{second}^{-1} \text{hour}^{-1}$, and
- a_0, a_1, a_2 = monthly regression coefficients,

provided a reasonable fit to the data for high runoff months (November 1972-April 1973, December 1973-April 1974). Parameters of these regression equations are given in Table 1. Highest correlation coefficients were obtained where there was a wide range of discharge and DMRP concentrations, and a statistical analysis shows all monthly equations different from one another at the 5% level of significance.

Monthly equations and bihourly discharge measurements were used to calculate DMRP lost from the watershed using Eq. 2.

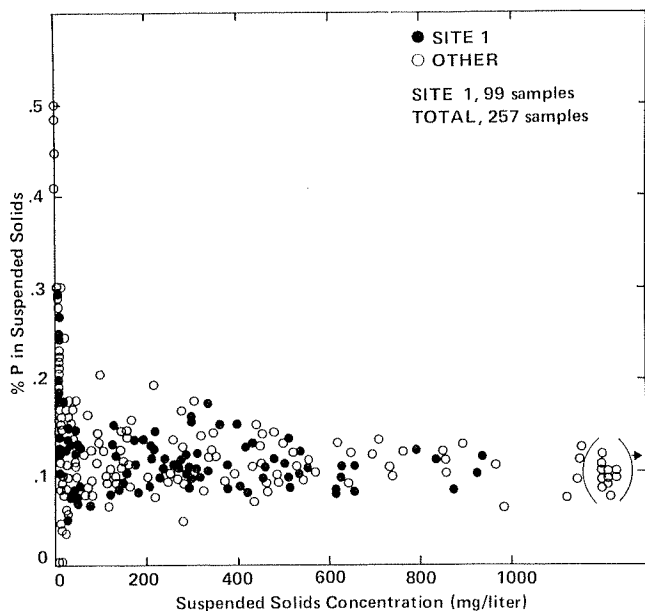
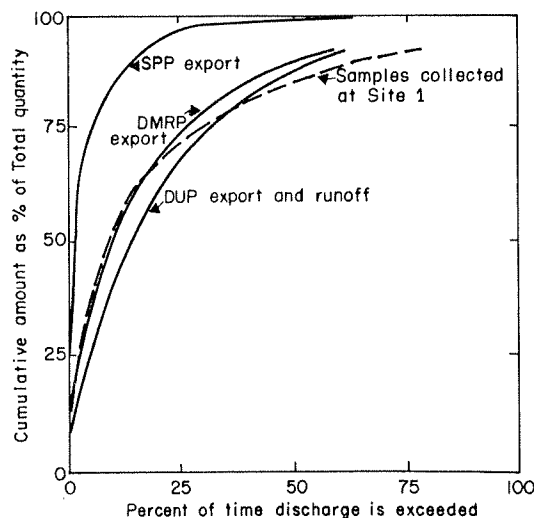
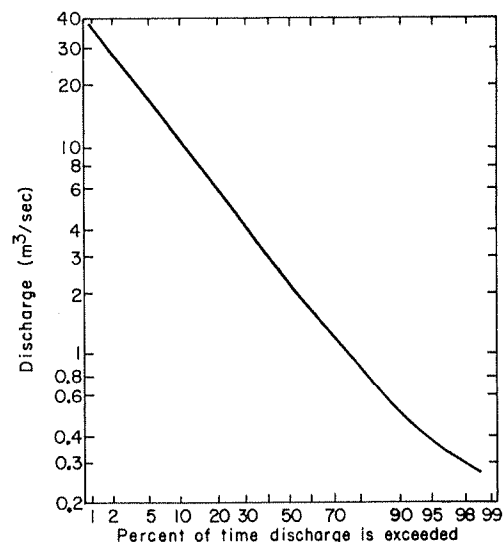


Fig. 3—Percent P in suspended solids plotted against the concentration of suspended solids. Dots represent samples collected at site 1, open circles represent samples collected elsewhere in the watershed.

Fig. 4—Flow duration (upper figure) and cumulative loss of P fractions, and water and cumulative number of samples collected plotted against flow duration (lower figure). Flow duration analysis determined from 50 years of data (U. S. Geol. Surv.). Export determined from data collected during the experimental period.

$$\Sigma \text{DMRP} = K \Sigma(Q)(a_0 + a_1 Q + a_2 \Delta Q / \Delta t) \quad [2]$$

where

ΣDMRP = kg of DMRP/month,

$K = 7.2 \times 10^{-3}$ which converts instantaneous flux to kg/2 hours,

Q = instantaneous bihourly discharge (m^3/second),

a_0, a_1, a_2 = monthly regression coefficients, and

$\Delta Q / \Delta t$ = bihourly rate of change of discharge ($\text{m}^3 \text{ second}^{-1} \text{ hour}^{-1}$).

The standard error was estimated by the variance as given in Eq. [3], assuming discharge was measured without error. Included in the variance are random errors in sampling, analysis, and lack of fit of the model.

$$\begin{aligned} \text{Var}(\Sigma \text{DMRP}) &= (K \Sigma Q)^2 \text{var}(a_0) + (K \Sigma Q^2)^2 \text{var}(a_1) \\ &+ [K \Sigma Q (\Delta Q / \Delta t)]^2 \text{var}(a_2) + 2(K \Sigma Q)(K \Sigma Q^2) \text{Cov}(a_0 a_1) \\ &+ 2(K \Sigma Q)[K \Sigma Q (\Delta Q / \Delta t)] \text{Cov}(a_0 a_2) \\ &+ 2(K \Sigma Q^2)[K \Sigma Q (\Delta Q / \Delta t)] \text{Cov}(a_1 a_2). \end{aligned} \quad [3]$$

In months with low discharge rates (October–November 1972, May–November 1973), DMRP concentrations were generally relatively low at site 1 and there was no significant correlation between discharge and DMRP concentration. DMRP lost during these months was estimated from Eq. [4], and the standard error was estimated from Eq. [5], assuming Q is measured without error.

$$\Sigma \text{DMRP} = \bar{c}(K \Sigma Q) \quad [4]$$

where \bar{c} = average of measured concentrations for each month, ($\mu\text{g P/liter}$), $K = 7.2 \times 10^{-3}$, and Q = bihourly discharge.

$$\text{Var}(\Sigma \text{DMRP}) = (K \Sigma Q)^2 \text{Var } \bar{c}. \quad [5]$$

The results are summarized in Table 3.

Table 1—Parameters in regression equations of DMRP on discharge and rate of change of discharge at site 1

Month	Year	n†	a_0	a_1	a_2	r †	Range of flow	
							Measured	Sampled
— m^3/second —								
Nov.	1972	28	16.6	0.56	1.68	0.91	1.6–69	1.7–66
Dec.	1972	15	16.4	0.27	0.42	0.91	3.7–81	6.8–78
Feb.	1973	9	22.7	0.21	0.48	0.73	1.8–61	4.4–60
Mar.	1973	26	13.8	0.16	0.65	0.34	3.4–45	4.8–38
Apr.	1973	17	6.0	0.50	3.92	0.82	4.4–52	4.4–44
Nov.	1972 to							
Apr.	1973	95	13.2	0.41	1.30	0.72	1.6–81	
Dec.	1973	81	9.8	0.88	1.58	0.69	1.3–48	1.5–38
Jan.	1974	39	12.4	0.42	0.21	0.46	2.2–41	3.6–23
Feb.	1974	38	13.2	0.43	1.93	0.81	2.0–47	3.5–46
Mar.	1974	43	9.6	-0.06	0.27	0.07	1.2–24	5.2–23
Apr.	1974	85	8.6	0.15	0.33	0.54	8.9–62	12.2–62
Dec.	1973 to							
Apr.	1974	286	13.1	0.13	0.86	0.26	1.2–62	
Nov.	1972 to							
Apr.	1974	381	12.3	0.26	1.38	0.48	1.2–81	

† n is number of observations, r is correlation coefficient.

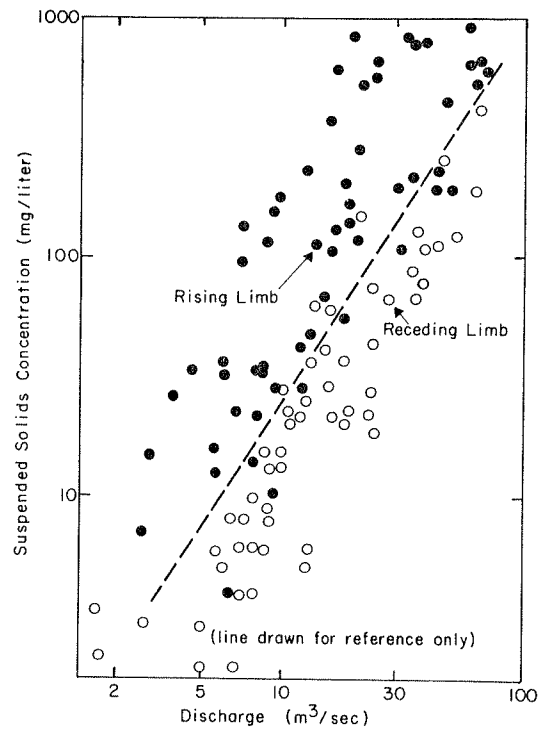


Fig. 5—Suspended solids concentration plotted against discharge at site 1 for the period September 1972 to April 1973. Dots represent samples collected when discharge was increasing (rising limb), and open circles represent samples collected when discharge was decreasing (receding limb).

DUP

There were no significant correlations of DUP concentrations on discharge except during November 1972 when there was a positive correlation. High runoff (November 1972–April 1973, December 1973–April 1974) and low runoff (September–October 1972, May–November 1973) periods were similar with respect to average concentrations and variability.

The average of measured DUP concentrations during low runoff months at site 1 was $11.5 \mu\text{g P/liter}$ and standard error of the mean was 0.8 for 215 samples. During high runoff months, average DUP concentration was $11.7 \mu\text{g P/liter}$ and the standard error of the mean was 0.7 for 308 observations. DUP loss was calculated from the seasonal (high runoff and low runoff periods) average concentration and discharge as in Eq. [4] and the standard error was calculated as in Eq. [5]. The results are summarized in Table 3.

SPP

At site 1, suspended solids concentrations for high flow months were correlated with discharge as shown in Fig. 5. For a given discharge, suspended solids concentration was higher during periods of increasing flow than during periods of decreasing flow, and monthly regression equations of the same form as Eq. [1] were fit to the data and parameters in the regression equations are shown in Table 2.

Since intercepts are negative ($a_0' < 0$), the calculations

Table 2—Parameters in regression equations of suspended solids on discharge and rate of change of discharge at site 1

Month	Year	a'_0	a'_1	a'_2	n †	r †	Q_{min} m ³ /second
Nov.	1972	-81.4	7.9	63.4	26	0.94	10.5
Dec.	1972	-50.0	6.1	35.5	23	0.97	8.5
Jan.-Feb.	1973	-59.5	13.2	87.1	18	0.96	5.0
Mar.	1973	-90.7	15.0	75.4	21	0.87	6.5
Apr.	1973	-22.2	4.3	28.0	18	0.92	5.5
Nov.	1972 to						
Apr.	1973	-17.8	6.1	64.0	106	0.86	
Dec.	1973	-20.3	11.0	69.2	23	0.74	2.5
Jan.-Feb.	1974	-52.1	13.1	143.0	16	0.99	4.5
Mar.	1974	-34.5	6.7	31.0	16	0.90	5.2
Apr.	1974	-15.3	4.7	72.7	35	0.80	3.5
Dec.	1973 to						
Apr.	1974	-14.9	6.2	117.2	90	0.79	
Nov.	1972 to						
Apr.	1974	- 9.7	6.3	71.5	196	0.81	

† n is number of observations, r is correlation coefficient.

were separated into two portions to avoid calculating negative loss rates at low discharge. For each monthly equation, an arbitrary discharge rate Q_{min} was selected, and for all bihourly discharge values below Q_{min} , suspended solids concentration was set equal to 21 mg/liter, the average measured concentration for all $Q < Q_{min}$ during the high discharge months. For $Q > Q_{min}$, monthly suspended solids loss and the standard error was calculated in the same manner as DMRP export (Eq. [2], and [3]). For $Q < Q_{min}$, equations analogous to Eq. [4] and [5] were used.

During low runoff months, the frequency distribution of measured suspended solids concentration was bimodal due to the sampling schedule. Suspended solids lost from the watershed and the standard error were approximated as in Eq. [4] and [5] for these periods.

Solid phase P export was calculated from seasonal (i.e., high discharge and low discharge months) average percent P measured at site 1, and the calculated suspended solids export for each period. The standard error was estimated from Eq. 6.

$$SE \Sigma SPP = [(\Sigma SS)^2 (s_{\bar{P}})^2 + (\bar{P})^2 (s_{\Sigma SS})^2]^{1/2} \quad [6]$$

Table 3—Summary of P transported out of the watershed by Fall Creek for the period September 1972 to April 1974

Month	Year	Discharge (m ³ × 10 ⁶)	DMRP		DUP		SPP		Labile P kg	Total					
			kg P	SE†	kg P	SE†	kg P	SE†							
Sept.-Oct.	1972	46	372‡	29‡	530	41	2,450‡	305‡							
May-Nov.	1973														
Nov.	1972	27.7	775	29	3,320	238	3,166	2,025							
Dec.	1972	40.9	944	38											
Jan.	1973	20.6	517§	38§											
Feb.	1973	16.6	432	27											
Mar.	1973	29.9	482	33											
Apr.	1973	32.3	523	46											
Dec.	1972	21.6	493	20											
Jan.	1974	18.4	305	14											
Feb.	1974	15.4	279	13											
Mar.	1974	21	188	18											
Apr.	1974	39.9	500	16											
Total		330.3	5,810								3,850		33,353	1,257	43,013 kg

† SE, standard error.

‡ Excludes one sample of 640 mg/liter suspended solids, 143 µg MRP/liter at a flow of 3 m³/second which is not representative of any appreciable fraction of the total runoff.

§ Calculated using February 1973 regression.

where

ΣSPP = loss of suspended solids (metric tons),

$(s_{\bar{P}})^2$ = variance of the mean %P in SS,

\bar{P} = mean %P in SS, and

$(s_{\Sigma SS})^2$ = variance of SS loss estimate.

LABILE PHOSPHORUS

Labile P lost from the watershed on the storm sediment was estimated from sorption experiments. Values for labile P measured on 17 samples ranged from 20–60 µg of labile P/g of sediment, with some dependence on length of storage. Determinations on five fresh samples indicated that 40 µg P/g sediment is a reasonable average estimate, and the labile P exported was calculated from total sediment loss and represents about 3% of the total P lost. No estimate of error was made.

Phosphorus lost from the watershed during the sampling period is summarized in Table 3.

"BACKGROUND" LEVELS

So-called "natural" or "background" levels are difficult to determine, since the geology, vegetation, and landscapes vary throughout the watershed. To evaluate ground-water P levels, samples were collected in the spring and summer from six water table observation wells established by the U. S. Geological Survey in gravel outwash at the southeast corner of the watershed. Depths to the water table ranged from 3 to 10 m in the spring. In addition, stream samples were collected from watershed 24 (Fig. 1), which is about 250 ha, and is covered by second growth forest. The soils were derived from acid till, and there is no human activity. Figure 6 summarizes the dissolved P concentrations in streams and ground water observed in these areas. Low flow samples at site 24 are presumed to be representative of ground-water seepage, and there was no tendency for TDP concentration to increase during periods of high flow. The overall average concentrations of DMRP and TDP in the samples from the wells and watershed 24 were 5 and 13 µg P/liter, respectively, and these values were used as estimates of dissolved P in

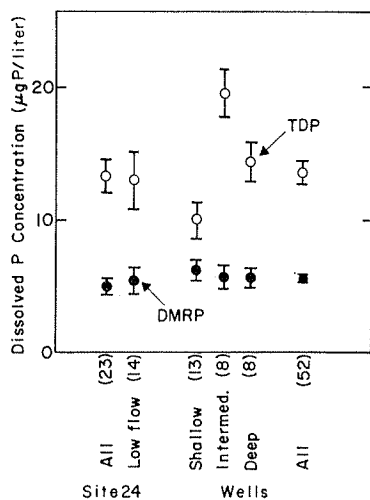


Fig. 6—Dissolved P concentrations in a stream draining a forested subwatershed and in ground water. Length of bar indicates \pm one standard deviation of the mean.

subsurface runoff throughout the watershed. A few springs and wells remote from houses and barns in other parts of the watershed showed similar values.

POINT SOURCES

Point sources of P located during this study include drainage from milking houses, domestic sewage from homes, and the municipal secondary sewage treatment plant at Dryden. In some cases, P levels in downstream reaches were strongly influenced by inputs from these point sources. For example below the Dryden sewage treatment plant, concentrations at low flow were often 10 to 20 times those above Dryden and in many other

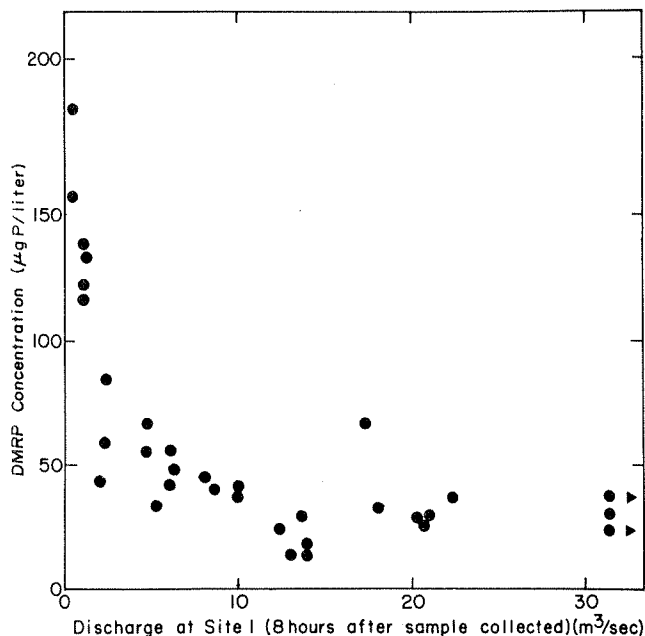


Fig. 7—DMRP concentration below the Dryden sewage treatment plant (site 2), February 1973 to September 1973 plotted against discharge measured at location one 8 hours later (travel time between the two sites is approximately 8 hours [Dunn, 1970]).

reaches of the stream. During high flow, concentrations below Dryden decreased markedly because of more extensive dilution (Fig. 7). Further studies of this as a model point source are given below.

During late September 1973, the flux of dissolved P at site 1 was about 0.2 kg per day, while a flux of 3.8 kg P/day was measured below the Dryden sewage treatment plant. During low flow periods, concentrations of dissolved P decreased downstream from major point source inputs, partly due to dilution, but there was also reaction of DMRP with the bottom sediments where it was stored. Figure 8 shows dissolved P flux, DMRP concentration, and bicarbonate extractable P in the bed sediment plotted against distance from the sewage treatment plant. The stream bed sediments act as a sink, accumulating inorganic P from point sources during low flow periods. Simple experiments indicated that these sediments will release P when stirred up during storm periods.

Mechanisms accounting for the loss of DUP from solution during transport have not been fully investigated. Other phenomena including biological uptake and chemical precipitation may also be causing transport losses, but these also remain uninvestigated.

INFLUENCE OF DIFFUSE SOURCE INPUTS OF DISSOLVED PHOSPHORUS

During storm periods, Fall Creek becomes a much more effective conduit for the transport of all P fractions, with daily loss rates of total P 1,000 to 10,000 times higher than those measured at low flow, since discharge and P concentrations each increase 1 or 2 orders of magnitude. Figure 9 shows details of storm periods sampled during November and December 1972 at site 1. The increase in

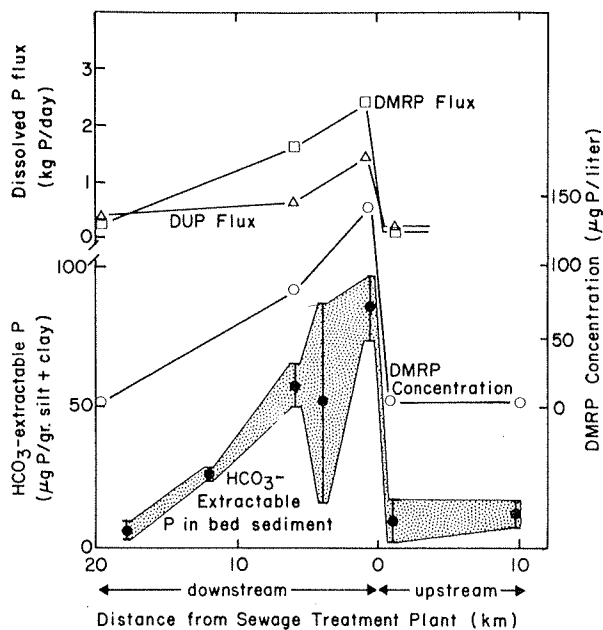


Fig. 8—Phosphorus levels at low flow (September to October 1973) above and below the Dryden sewage treatment plant. Length of bars (HCO_3^- -extractable P data) indicates \pm 2 standard deviations of the mean of 4 samples collected at each location. Concentration and discharge measurements were made over a 5-day period.

DMRP concentration with increasing discharge rate during periods of storm runoff is clearly shown, and there is evidence that two processes contributed to the increased concentrations observed during these events—inputs from surface runoff and release from streambed sediments.

Figure 10 shows the details of a storm in June 1973 sampled at site 1. The hump on the rising limb of the hydrograph coinciding with the high DMRP concentration was considered to be a pulse of surface runoff resulting from the thunderstorm. The peak P concentration reached site 1 too quickly after the beginning of the storm to have been generated from desorption, since the site of major P accumulation in the streambed is some 15–20 km upstream.

The empirical method of Chow (1964) was used to separate a portion of flow defined as surface runoff from all single-peak storm hydrographs. In the Fall Creek watershed, this probably represents water that reaches tributaries quickly through permeable glacial outwash, runoff from roads, road ditches, and villages as well as overland flow. Five single-peak storms from the winter of 1972–73 and three from the 1973–74 winter were analyzed in this manner. Figure 11 shows that DMRP concentrations are reasonably well correlated with the ratio of surface runoff to total runoff, as defined by this operational procedure.

Extrapolation of the data in Fig. 11 gives estimated DMRP concentrations of 61 and 36 $\mu\text{g P/liter}$ in the surface runoff for the first and second winters, respectively. A phosphate detergent ban went into effect in June 1973, between the two winters, and inputs of P from domestic sewage were reduced by about 50%. It is hypothesized that the difference between the two winters was due primarily to the reduced amount of P stored in the streambed from point sources during the second year. In other words, desorbed P as well as inputs of DMRP in surface runoff probably both caused the increased DMRP levels during storms as shown in Fig. 9 and 11 and the effects

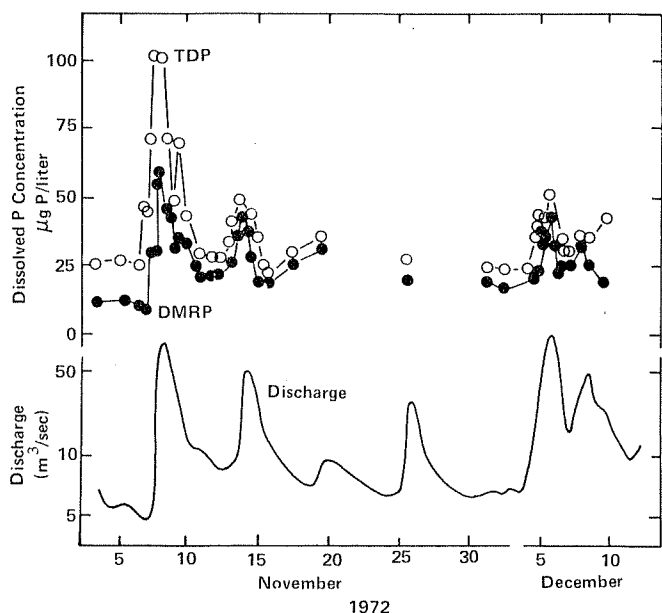


Fig. 9—Discharge and dissolved P concentrations at site 1, November to December 1972.

of each are not separable. As an estimate of DMRP in surface runoff, the 1972–73 data was used (36 $\mu\text{g P/liter}$). This is probably an overestimate since release from the bed sediments probably accounted for some portion. Since there was no apparent effect of surface runoff on DUP levels, the concentration of this fraction in surface runoff was estimated to be 12 $\mu\text{g P/liter}$, the average DUP concentration. Therefore, TDP concentration in surface runoff is estimated to be 48 $\mu\text{g P/liter}$.

Quantities of Dissolved Phosphorus

BACKGROUND PHOSPHORUS

The amount of dissolved P which would leave the watershed in the absence of human activity was estimated as the product of total water output and average concentration of dissolved P in the samples from the undisturbed watershed and the wells. For the whole watershed this amounts to about 4,300 kg of dissolved P or about 45% of the total amount of dissolved P which is transported out of the watershed by Fall Creek (Table 3, DMRP + DUP).

DIFFUSE SOURCE PHOSPHORUS

Inputs of dissolved P from diffuse sources were estimated in two ways. First, the estimated concentration of 48 $\mu\text{g dissolved P/liter}$ as derived above, and the esti-

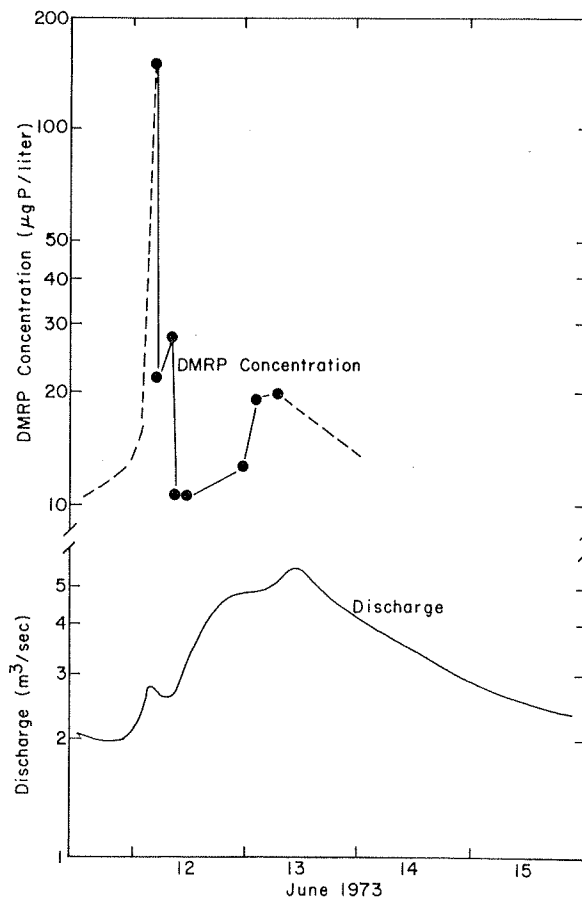


Fig. 10—Details of June 1973 storm. Data were collected at site 1.

mated surface runoff for the observation period (12% of the total) gave a calculated 1,900 kg of dissolved P delivered in the surface runoff (19% of the total dissolved P lost from the watershed). The second method is in reasonable agreement and is based primarily on soils data and plot runoff studies. About 10,000 ha of the watershed is cropped (mostly corn (*Zea mays* L.), hay, and small grains). Based on soil survey information and a survey of 20% of the farms, 40% of the cropland has a low potential for surface runoff, 34% has a medium potential, and 26% has a high potential for surface runoff (personal communication, J. J. Jacobs, Agric. Econ. Dep., Cornell Univ.). During the observation period, the total runoff averaged about 1 m per unit area. Of this, an average of 12 cm was estimated to be derived from surface runoff by the hydrograph analysis method. Somewhat arbitrarily, this surface runoff was distributed as 12 cm for the cropland with medium potential and 30 cm for the cropland with high potential for surface runoff. For 6 years, dissolved P concentrations in surface runoff from experimental plots receiving manure and fertilizer were monitored at Aurora, New York. Based on this data (personal communication, P. J. Zwerman and S. D. Klausner, Agron. Dep., Cornell Univ.), the concentration of TDP in the surface runoff was estimated at 80 µg P/liter (standard deviation of the sample = 20, standard error of the mean = 5) for cropland unmanured in the current year. Likewise 460 µg TDP/liter (standard deviation of sample = 103, standard error of the

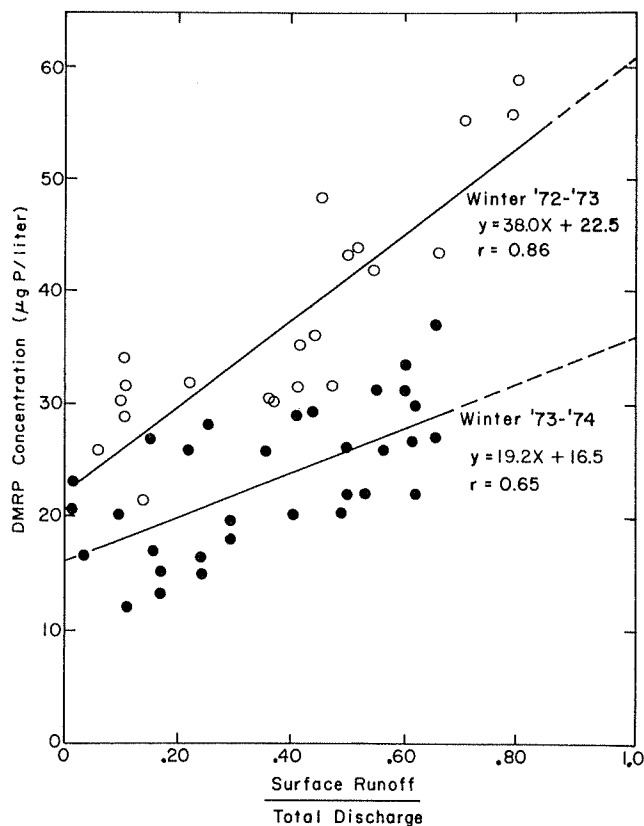


Fig. 11—DMRP concentration plotted against the ratio surface runoff/total discharge. Includes data from five storms in 1972-73 and three storms in 1973-74, r = correlation coefficient. Equations are different at the 5% level.

Table 4—Estimated diffuse source TDP from cropland

Manure	Surface runoff potential†	Area	Surface runoff	Micrograms TDP/liter‡	Loss
		ha	m ³ /ha		kg TDP
Yes	Low	1,200	0	--	--
Yes	Medium	1,050	1,200	445	560
Yes	High	800	3,000	445	1,070
No	Low	2,800	0	--	--
No	Medium	2,350	1,200	65	180
No	High	1,700	3,000	65	330
Total					2,140

† Low—Howard, Bath, Valois soil series; Medium—Mardin, Langford soil series; High—Lordstown, Volusia, Erie soil series.

‡ Concentration in excess of assumed background level.

mean = 63) was estimated for cropland manured in the current year.

The manure from 6,800 dairy cows was assumed to be spread on 3,100 ha of cropland and randomly distributed among the drainage classes described above. From these data about 2,100 kg of TDP were estimated to have been lost from cropped land. The data are summarized in Table 4.

Some additional inputs from barnlots are likely. Concentrations of TDP were measured in 35 samples taken above and below a barnlot. The concentrations of dissolved P averaged 8 µg P/liter greater below the barnlot (standard error of the mean = 2 µg P/liter) and, estimating the runoff as 1 m per unit surface area, the estimated loss from the barnlot was 56 kg dissolved P. This barnlot is adjacent to the stream which is the only source of water for the 35 or so cows. The feed bunkers were about 20 m from the edge of the stream and this situation was such as to maximize P loss to the stream. Considering the location of the other barnlots in the watershed, about 300 kg dissolved P was estimated to be contributed from these sources. The total P loss from agricultural land runoff (cropland plus barnlots) was estimated at about 2,400 kg by these methods, which was in fair agreement with the hydrograph method.

POINT SOURCE CONTRIBUTIONS

Dissolved P attributed to point sources was estimated by difference to be about 3,300 kg or 34% of the dissolved P lost during the observation period. However, actual inputs to the stream would appear to have been somewhat greater considering inputs from the sewage treatment plant (2,800 kg as estimated from discharge measurements and about 60 samples collected above and below the plant) and failing septic systems. About 4,000 people not on sewer lines live within 1 km of a major tributary and in a survey of one village (personal communication, H. R. Capener, Dep. of Rural Sociol., Cornell Univ.), half of the disposal fields were found to be inoperative. About 400 kg of dissolved P was contributed by this village during the observation period.

Illustrated in Fig. 12 are weighted mean concentrations and P flux for several sites in the major subwatersheds for the period May 1973 through April 1974. Numbers in parentheses are estimated based on the average values for the watersheds above sites 4, 21, and 15. For the streams

PHOSPHORUS BALANCE

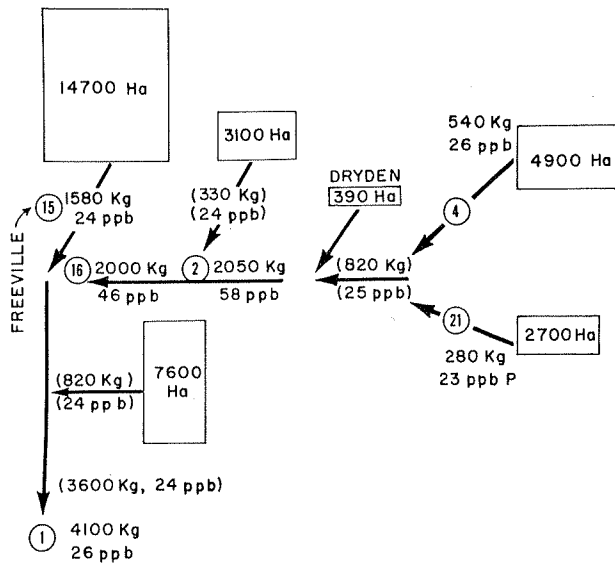


Fig. 12—Schematic diagram of Fall Creek Watershed showing weighted mean concentration of TDP at several sites for the period May 1973 to April 1974. Circles represent sampling sites as shown in Fig. 1. Concentrations in parentheses are estimated from the values obtained at sites 4, 15, and 21 which drain areas of similar land use and topography.

above these sites (2/3 of the whole watershed), the weighted mean concentration was 24 µg TDP/liter. If the inputs from the remaining 1/3 of the watershed were the same, the total dissolved P flux at site 1 would be:

$$\begin{aligned}
 &(24 \mu\text{g TDP/liter} \times 150 \times 10^6 \text{ m}^3 \text{ of runoff} = 3,600 \text{ kg}) \\
 &+ 1,200 \text{ kg from the sewage treatment plant} \\
 &+ \text{an estimated 1,700 kg of domestic sewage} \\
 &= 6,500 \text{ kg dissolved P.}
 \end{aligned}$$

This assumes that 1/2 of the septic systems of people living near the stream are failing. Comparison to the measured dissolved P loss of about 4,100 kg indicates that transport losses were probably important. The exact nature of the processes involved is unclear, but incorporation into the biota and reaction with the stream bed sediment are likely to be important.

A summary of P sources is given in Table 5 for the experimental period September 1972 to April 1974. No attempt was made to estimate an average yearly loading because of the marked differences between years.

Table 5—Estimated sources of dissolved P transported out of the watershed by Fall Creek during the period September 1972 to April 1974

Source	How determined	Kg P	Percent of total
Background	Samples at site 24 and well samples	4,300	44
Diffuse sources in surface runoff	Hydrograph analysis procedure and extrapolation from plot studies.	2,100	22
Point sources	By difference	3,300	34
Total	Table 3, DMRP + DUP	9,700	100

Even though relatively large quantities of P are used in agricultural operations, most of the soluble P released to the landscape remains in the soil. Survey information (personal communication, J. J. Jacobs, Dep. of Agric. Econ., Cornell Univ.) indicates that more than 240,000 kg of soluble P was applied to the land in manure and fertilizer. Inputs of dissolved P in precipitation were estimated to be about 17,000 kg (personal communication, S. D. Klausner, Dep. of Agron., Cornell Univ.) and decaying vegetation probably provides a sizeable pool of soluble P potentially available for loss in surface runoff. The estimate of dissolved P from diffuse sources indicates that < 1% of the soluble P that went onto the landscape during the observation period was lost in dissolved form.

In assessing the overall P balance, about six times as much P was released to the watershed from sewage, precipitation, and agricultural operations during the observation period as was transported out of the watershed by the stream as dissolved P plus particulate P.

SUMMARY

The P losses by stream transport in Fall Creek, which drains a rural watershed in central New York, were studied over a 20-month period. Samples were collected from Fall Creek at several locations over a range of discharge conditions. Sampling efforts were concentrated during storm runoff periods. Estimates of P loss were obtained, and estimates of the standard errors were calculated.

Phosphorus loss associated with the suspended solids accounted for 78% of the total exported, and dissolved inorganic and organic fractions accounted for 14 and 8%, respectively.

Estimates of sources of dissolved P indicate that about 44% was derived from biogeochemical processes, about 22% was derived from diffuse sources, and the remaining 34% was derived from point sources, mostly domestic sewage.

There was a transmission loss of dissolved P which occurs during low flow periods which affected point source inputs, particularly those from the sewage treatment plant. Some of the inorganic P was stored in the stream bed sediments and, coupled with inputs from diffuse sources in the surface runoff, P released from the stream-bed sediment caused increased concentrations of DMRP at most sampling sites during storm periods.

The results from this study demonstrate that the landscape is effectively accumulating P, and < 1% of the P applied to the landscape as fertilizer and manure, in soluble form, leaves the watershed in dissolved form.

In addition to using suitable storage and analytical procedures, the scheduling of sample collection is important for obtaining representative watershed data. Storm runoff periods must be sampled to obtain an accurate estimate of P loss. In the case of Fall Creek, about 75% of the total P was exported in the 10% of the observation period during which the highest flow occurred.

If the flux of some constituent is calculated from total discharge and the average concentration of that constituent

ent in samples taken at random or on a fixed schedule, low flow concentrations will be most heavily weighted, since flow is relatively low most of the time. If there is a dependence of concentration on discharge, the flux so determined will be too low if concentration is directly related to discharge (Fig. 2), and too high if the relationship is inverse (Fig. 7). The degree of dependence (slope of the regression) and nature of the flow duration distribution will determine the magnitude of the error. In the study reviewed here, the errors in loss calculated in such a way would range from slight in the case of DUP, where there is no dependence on discharge to severe in the case of SPP and suspended solids, where concentration increases markedly with discharge.

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Uptake of Cadmium by Soybeans as Influenced by Soil Cation Exchange Capacity, pH, and Available Phosphorus¹

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ABSTRACT

The accumulation of cadmium (Cd) and its effect on vegetative growth of soybeans (*Glycine max* [L.] Merr. var. Amsoy) in soils with a range in cation exchange capacity (CEC), pH, and available phosphorus (P) were investigated in greenhouse experiments. Cadmium uptake decreased as soil pH and CEC increased, while increasing available soil P was related to increased Cd accumulation. Cadmium extracted from the soil by Bray P₁ reagent, Bray P₂ reagent, 2N MgCl₂, and 0.1N EDTA was significantly correlated with plant Cd concentrations. The growth of the soybean shoots was generally depressed when tissue concentrations reached 3-5 µg Cd/g dry weight. Cadmium uptake by soybeans was correlated with the ratio of added Cd to the Cd sorptive capacity of soil.

Additional Index Words: soil extractants, cadmium sorption, heavy metal pollution.

Recent concern for the involvement of Cd in human health problems such as hypertension (Schroeder, 1965), emphysema and chronic bronchitis (Lewis et al., 1969), and other diseases has initiated studies relating to many aspects of Cd in the environment. Elevated environment-

al levels of Cd may come from a variety of sources such as smelting industries (Buchauer, 1973), impurities in agricultural chemicals (Barrows, 1966), sewage sludge (Jones et al., 1973), and attrition of automobile tires (Lagerwerff and Specht, 1970). Levels in soil in excess of 1,700 µg Cd/g of soil have been reported near Zn smelters (Buchauer, 1973), and Lagerwerff and Specht (1970) found up to 1.82 µg Cd/g of soil close to highways.

In view of the importance of plants in most food chains (both natural and agricultural), a number of studies have recently been directed towards plant accumulation and effects of Cd. Various plants such as corn (*Zea mays* L.), tomato (*Lycopersicon esculentum*), radish (*Raphanus sativus*), and Swiss chard (*Beta vulgaris cicla*) efficiently accumulate Cd from nutrient solutions (Page et al., 1972; Tumer, 1973; Root et al., 1975). Hydroponic solution concentrations of 1 µg/ml led to substantial uptake and the depression of yield of vegetative portions of the plants. Cadmium uptake from soil systems has also been studied (e.g., Lagerwerff, 1971; John et al., 1972; Jones et al., 1973; Haghiri, 1973). With wheat (*Triticum aestivum*) and soybeans grown in a silty clay loam soil, visual symptoms of Cd toxicity began to occur at 2.5 µg Cd/g of soil (Haghiri, 1973).

The soil factors affecting Cd uptake by plants have been investigated by several workers. Lagerwerff (1971) reported a slight increase in Cd uptake by radish tops and roots due to reduction of the soil pH from 7.2 to 5.9. The Cd concentration in oat shoots (*Avena sativa*) was re-

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